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(54) **Flame-resistant propylene polymer compositions containing bismuth carbonate and a brominated aromatic compound.**

(57) Disclosed is a flame-resistant propylene polymer composition comprising:
(A) 30 to 60% of a propylene polymer material;
(B) 5 to 15% of a bismuth carbonate;
(C) 15 to 40% of a brominated aromatic compound; and optionally, (D) 20 to 30% of talc.
The compositions are useful in the manufacturing of injection molded articles.

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This application relates to flame retardant polyolefin compositions containing a flame retardant admixture. In particular, propylene polymer compositions containing a flame retardant admixture of bismuth carbonate and a brominated aromatic compound.

Various methods to provide polyolefin materials with flame-resistance are known in the art. For example, U.S. 4,010,139 discloses a self-extinguishing polyolefinic composition containing (a) a polyolefin selected from the group consisting of homopolymers and copolymer of ethylene, alpha-olefins and styrene; and (b) a mixture of: (1) a bismuth compound selected from the group consisting of basic bismuth carbonate and triphenyl-bismuthine; and (2) a partially halogenated compound which is capable of breaking down in the presence of heat to form the corresponding halogen halide.

B1 4,710,528 (Reexamined U.S. 4,710,528) describes flame resistant thermoplastic polymeric compositions comprising (A) from 60 to 98.9% of a thermoplastic polymer; (B) from 0.1 to 10% of an antimony and/or bismuth compound; (C) 0.05 to 1% of a promoter of free radicals; and (D) from 1 to 35% of a melamine bromohydrate.

U.S. 4,203,882 discloses impact resistant polymer compositions having flame-resistance properties comprising (1) a blend of a thermoplastic block propylene-ethylene copolymer and an elastomeric ethylene-propylene copolymer; (2) 0.5 to 5% of basic bismuth carbonate ($\text{BiO})_2\text{CO}_3$; (3) 0.3 to 1.3% of a triazine compound; (4) 2 to 10% of a chlorinated paraffin wax; and (5) 0.5 to 10% of a bromine containing organic compound.

U.S. 5,079,283 discloses a flame-retardant polypropylene composition comprising a modified polypropylene-based polymer, antimony oxide or sodium antimonate and a halogenated organic compound or a phosphorous containing compound.

U.S. 5,166,235 discloses concentrates of a flame retardant additives, in the form of nonextruded particles, of which each one comprising (A) a matrix of a nonextruded, as polymerized particle of a polymer or copolymer of olefins having porosity greater than or equal to 15%, expressed as a percent of the void volume on the total volume of the particle, (B) the product of reaction between bismuth or antimony trichloride or tribromide, or their mixtures, and one or more amines; wherein said product (B) is made "in situ" and deposited on the surface of the matrix and inside the pores thereof.

SU 1052518 describes a flame-resistant polypropylene composition containing 100 parts of polypropylene, 3-8 parts of basic bismuth carbonate, 2-4 parts of a halogen containing compound, such as decabromodiphenyl oxide, hexabromobenzene, and 0.2 to 0.8 parts of a phenolic antioxidant.

It has been found that polyolefin compositions, in particular propylene polymer compositions can reach excellent levels of flame resistance when blended with an admixture of bismuth carbonate and a brominated aromatic compound.

Accordingly, this invention provides flame-resistant propylene polymer compositions comprising:

- (A) 30 to 60% of a propylene polymer material;
- (B) 5 to 15% of a bismuth carbonate;
- (C) 15 to 40% of a brominated aromatic compound; and optionally, (D) 20 to 30% of talc.

All parts and percentages used in this application are by weight unless otherwise specified. Ambient or room temperature is approximately 25 °C.

The propylene polymer material used in the present invention can be (i) a propylene homopolymer having an isotactic index greater than 80, preferably from 85 to 98, (ii) a random copolymer of propylene and an olefin selected from ethylene or C_4 - $_{10}$ alpha-olefins, provided that, when the olefin is ethylene, the maximum polymerized ethylene content is about 10%, preferably 4-9%, and when the olefin is a C_4 - $_{10}$ alpha-olefin, the maximum polymerized content thereof is about 20%, preferably about 16%; (iii) a random terpolymer of propylene with two alpha-olefins selected from the group consisting of ethylene and C_4 - $_{8}$ alpha-olefin, provided that the maximum polymerised C_4 - $_{8}$ alpha-olefin content is about 20%, preferably about 16%, and when ethylene is one of said alpha-olefins, the maximum polymerized ethylene content is about 5%, preferably about 4%, (iv) a homopolymer of (i) or a random copolymer of (ii) impact modified with from about 5 to 70% of an ethylene-propylene copolymer rubber, or an ethylene-propylene-non-conjugated diene monomer rubber having a diene content of about 2-8%, and an ethylene content of from 7 to 70%; or (v) mixtures thereof.

The C_4 - $_{10}$ alpha-olefins include linear or branched C_4 - $_{10}$ alpha-olefins such as 1-butene, 1-pentene, 4-methyl-1-pentene, 3-methyl-1-butene, 1-hexene, 3,4-dimethyl-1-butene, 1-heptene, 3-methyl-1-hexene, 1-octene, and the like.

Preferably, the polymer material is polypropylene, an ethylene-propylene copolymer rubber impact modified polypropylene or mixture thereof.

Suitable bismuth carbonates useful in the present invention include $(\text{BiO})_2\text{CO}_3$ and $\text{Bi}_2\text{O}_3\text{CO}_2 \cdot 1/2\text{H}_2\text{O}$. Preferred is $\text{Bi}_2\text{O}_3\text{CO}_2 \cdot 1/2\text{H}_2\text{O}$. The brominated aromatic compound which can be used in the compositions

of this invention include decabromodiphenyl oxide, octabromodiphenyl oxide and pentabromodiphenyl oxide. The preferred brominated aromatic compound is decabromodiphenyl oxide.

The talc, when present in the composition of the present invention, can be any convention talc.

Preferably, the propylene polymer material is present in an amount of from 35 to 45%, the bismuth carbonate is present in an amount of from 7 to 12%, the brominated aromatic compound is present in an amount of from 20 to 30%, and the talc is present in an amount of from 20 to 25%.

In addition to the above main ingredients, the composition of the invention contains from 0.10 to 5% of additives such as antioxidants, ultraviolet absorbers, thermal stabilizers, flow agents, antistatic agents, mold release agents, inorganic fillers and/or pigments.

The compositions of the present invention can be prepared according to conventional methods, for example by mixing the propylene polymer material, bismuth carbonate, brominated aromatic compound and the talc, as well as known additives in a blender such as a Henschel or Banbury mixer, to uniformly disperse the ingredients, at a temperature equal or exceeding the polymer softening temperature, then extruding the mixture and pelletizing.

The present invention will be illustrated in greater detail with reference to the examples of the invention set forth below. The test samples and physical properties of the following working examples and comparative examples were prepared and measured according to the following methods:

Melt Flow, g/10 min.	ASTM D-1238
Specific Gravity, g/cm ³	ASTM D-729A
Flexural Modulus, psi	ASTM D-790
Tensile Strength, psi	ASTM D-638
Tensile Elongation, %	ASTM D-638
HDT, 66 psi, °C	ASTM D-648
264 psi, °C	
Gardner Falling Dart Impact, in-lb.	ASTM D-3029
Notched Izod, ft-lb/in.	ASTM D-256A
Tool Shrink parallel, in/in.	ASTM D-955
perpendicular, in/in.	

To determine the flame retardancy properties of the compositions, test samples (0.125 in.) are molded at 200 °C - 240 °C on a 75 ton Van Dorn type molding press.

The level of flame-resistance of the samples is determined both by measuring the oxygen index according to the ASTM D-2863, and by applying UL 94 standards (issued by Underwriter Laboratories-USA).

The oxygen index, (LOI), measure represents the minimum concentration of oxygen (expressed in % vol) in an oxygen-nitrogen mixture which allows the sample of the material being examined, after having been ignited, to burn continuously for 3 minutes and/or for 50 mm of the length of the sample.

The UL 94 test is conducted on samples which are positioned vertically and have the thickness indicated in the test method. From the moment that the flame source is removed, observed is the time it takes for the sample to extinguish and whether the material drips or not during combustion. This test classifies the materials (1) V-0 when the average extinguishing time of the flame is less than or equal to 5 seconds, (2) V-1 when the average extinguishing time of the flame is less than or equal to 25 seconds, and (3) V-2 when it behaves like V-1, and also drips droplets of lighted melted polymer capable of igniting cotton located 305 mm under it.

The compositions of the present invention are prepared by mixing propylene polymer material, bismuth carbonate, brominated aromatic compound, talc, and additives in a Banbury mixer, until the ingredients are uniformly disperse, at a temperature equal or exceeding the polymer softening temperature, then the mixture is extruded and pelletized. The pellets are molded, cooled and removed for testing.

The ingredients used in the preparation of the compositions of this invention illustrated in the examples that follow are:

- Polymer A - an ethylene-propylene copolymer rubber impact modified polypropylene, 30.7% EPR content, 21.5% ethylene content and MFR of 9 dg/min.;
- Polymer B - an ethylene-propylene copolymer rubber impact modified polypropylene, 13.4% EPR, 8.5% ethylene content and MFR of 35 dg/min.;

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Polymer C - an ethylene-propylene copolymer rubber impact modified polypropylene, 13.7% EPR, 9% ethylene content and MFR of 4 dg/min.;

Polymer D - a propylene homopolymer, MFR of 22 dg/min.;

Polymer E - an ethylene-propylene copolymer rubber impact modified ethylene-propylene random copolymer, 33% EPR content, 22% ethylene content and MFR of 10.5 dg/min..

Cantal 45/90 10 micron talc from Canada Talc Industries Ltd.

Colonial 3300 N110 50% carbon black masterbatched in low density polyethylene from Colonial Rubber Works Inc.

Epon 1002 Epoxy bisphenol A epoxide from Shell Chemical Company.

Irganox 1010 tetrakis[methylene(3,5-di-tert-butyl-4-hydroxyhydrocinnamate)]methane stabilizer from Ciba-Giegy.

Irganox B-225 50:50 blend of Irganox 1010 and Irgafos 168, tris(2,4-di-tert-butylphenyl)phosphite, stabilizer from Ciba-Giegy.

DSTDP a distearylthiodipropionate.

Examples 1 and 2

The ingredients of the compositions of present invention of each example are illustrated in Table 1 are prepared according to the general procedure described above.

The physical properties are set forth in Table 1.

Table 1

Ingredients	Examples	
	1	2
Polymer A	41.00	37.95
Bismuth subcarbonate	7.25	8.40
Decabromodiphenyl	23.00	25.00
Cantal 45/80 Talc	22.60	23.00
Irganox 1010	0.10	0.10
Irganox B-225	0.30	0.30
Calcium Stearate	0.10	0.10
Epon 1002 Epoxy	0.75	0.75
DSTDP	0.40	0.40
Colonial 3300 Black	4.00	4.00
Properties		
Specific Gravity, g/cm ³	1.47	1.48
Melt Flow, g/10 min	4.8	4.5
Flexural Modulus, psi	240000	241000
Tensile Strength, psi	2161	2203
Tensile Elongation, %	9.7	14.3
HDT, 66 psi, °C	97	99
264 psi, °C	51	53
Gardner Falling Dart Impact, in-lb.	120	120
Notched Izod, ft-lb/in	0.91	0.79
LOI, %	27	30
UL 94, Vertical Burn	V-0	V-0

As demonstrated by the results in Table 1, the compositions of Examples 1 and 2 obtained UL 94 ratings of V-0.

Examples 3-6

The ingredients of the compositions of each example illustrated in Table 2 are prepared according to the general procedure described above 2.

The properties are set forth in Table 2.

Table 2

Ingredients	Examples			
	3	4	5	6
Polymer B	19.27	—	—	—
Polymer C	19.28	—	8.55	—
Polymer D	—	23.55	—	23.35
Polymer E	—	15.00	30.00	16.00
Bismuth subcarbonate	7.80	7.80	7.80	7.80
Decabromodiphenyl	25.00	25.00	25.00	25.00
Cantal 45/80 Talc	23.00	23.00	23.00	23.00
Irganox 1010	0.10	0.10	0.10	0.10
Irganox B-225	0.30	0.30	0.30	0.30
Calcium Stearate	0.10	0.10	0.10	0.10
Epon 1002 Epoxy	0.75	0.75	0.75	0.75
DSTDP	0.40	0.40	0.40	0.40
Colonial 3300 Black	4.00	4.00	4.00	4.00
Mark 645A*	—	—	—	.20
Properties				
Specific Gravity, g/cm ³	1.52	1.52	1.52	1.51
Melt Flow, g/10 min	3.1	9.5	6.7	8.8
LOI, %	28	29	29	29
UL 94, Vertical Burn	V-0	V-0	V-0	V-0

* A dibutyl maleate blend from Argus.

It can be seen from the results in Table 2, that the compositions of the present invention, Examples 3-6 obtained UL 94 ratings of V-0.

The compositions of the present invention are useful for the production of injection molded articles such as battery cases, electrical boxes or housings and connectors.

Other features, advantages and embodiments of the invention disclosed herein will be readily apparent to those exercising ordinary skill after reading the foregoing disclosures. In this regard, while specific embodiments of the invention have been described in considerable detail, variations and modifications of these embodiments can be effected without departing from the spirit and scope of the invention as described and claimed.

Claims

1. A propylene polymer composition having improved flame resistance consisting essentially of:

- (A) 30 to 60% of a propylene polymer material selected from the group consisting of (i) a propylene homopolymer having an isotactic index greater than 80, (ii) a random copolymer of propylene and an olefin selected from ethylene or C₄₋₁₀ alpha-olefins, (iii) a random terpolymer with two alpha-olefins selected from the group consisting of ethylene and C₄₋₈ alpha-olefin, (iv) a homopolymer of (i) or a random copolymer of (ii) impact modified with from about 5 to 70% of an ethylene-propylene copolymer rubber, or an ethylene-propylene-non-conjugated diene monomer rubber having a diene content of about 2-8%, and an ethylene content of from 7 to 70%; or (v) mixtures thereof;
- (B) 5 to 15% of a bismuth carbonate selected from the group consisting of (BiO)₂CO₃ and Bi₂O₃ CO₂ 1/2H₂O;
- (C) 15 to 40% of a brominated aromatic compound selected from the group consisting of decabromodiphenyl oxide, octabromodiphenyl oxide and pentabromodiphenyl oxide; and optionally,
- (D) 20 to 30% of talc.

2. The composition of claim 1, wherein said bismuth carbonate is material is Bi₂O₃ CO₂ 1/2H₂O.

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3. The composition of claim 2, wherein said talc is present in an amount of from 20 to 25%.
4. The composition of claim 3, wherein said bismuth carbonate is present in an amount of from 7 to 12%.
- 5 5. The composition of claim 4, wherein said brominated aromatic compound is decabromodiphenyl oxide.
6. The composition of claim 5, wherein said decabromodiphenyl oxide is present in an amount of from 20 to 30%.
- 10 7. The composition of claim 1, wherein (A) is from 35 to 45%, (B) is from 7 to 12%, (C) is from 20 to 30% and (D) is from 20 to 25%.
8. The composition of claim 7, wherein (A) is an ethylene-propylene rubber copolymer impact modified polypropylene having an EPR content of 30.7%, an ethylene content of 21.5% and MFR of 9 dg/min.
- 15 9. The composition of claim 8, wherein (B) is $\text{Bi}_2\text{O}_3\text{CO}_2 1/2\text{H}_2\text{O}$.
10. The composition of claim 9, wherein (C) is decabromo-diphenyl oxide.

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EUROPEAN SEARCH REPORT

Application Number
EP 94 10 4260

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
A,D	FR-A-2 407 238 (MONTEDISON) * page 3, line 4 - line 8 * * page 5, line 9 - page 6, line 1 * * tables I,II,III * * claims 1,3 * ---	1,4,5	C08K3/26 C08K5/06 C08L23/10
A	US-A-5 116 898 (R.A. SCHLEIFSTEIN) * column 1, line 25 - line 30 * * column 2, line 25 - line 28 * * examples I-IV * * claims 1,4 * -----	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
			C08K
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 14 July 1994	Examiner Engel, S
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application I : document cited for other reasons & : member of the same patent family, corresponding document			